Electron currents from ~~Born-Oppenheimer~~ Complete Adiabatic wavefunctions

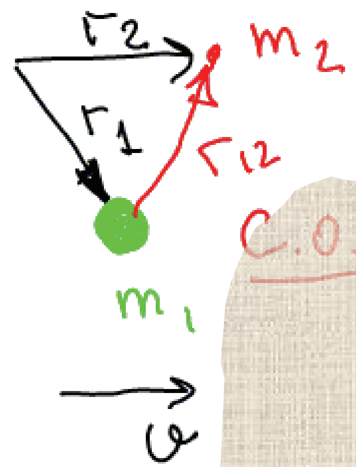
Serguei Patchkovskii

SaD Technologies, NRC Canada, Ottawa, Canada

Game plan for the next 34¾ minutes

- Nuclear motion on a single Born-Oppenheimer potential energy surface does not induce an electron current
- A toy example: electron current for a peripatetic Hooke's atom
- Electron current and a single-surface time-dependent Born-Oppenheimer wavefunction
  - expectation value
  - continuity relations
- Refresher: Born-Huang Ansatz
- Treating electron currents
  - general case: Born-Huang w.f.
  - special case: Born-Oppenheimer w.f.
- Numerical implementation
- Examples
- Conclusions: Complete Adiabatic w.f.s and femtosecond dynamics

Hooke's atom



$$\hat{H}(\vec{r}_1,\vec{r}_2) = -\frac{1}{2m_1}\hat{\Delta}_1 - \frac{1}{2m_2}\hat{\Delta}_2 + \frac{k}{2}|\vec{r}_1-\vec{r}_2|^2$$

C.O.M: $\vec{r}_1 = \vec{R} - \frac{m_2}{m_1+m_2}\vec{r}_{12}$ $\qquad \vec{r}_2 = \vec{R} + \frac{m_1}{m_1+m_2}\vec{r}_{12}$

$$\frac{\partial}{\partial \vec{r}_1} = -\frac{\partial}{\partial \vec{r}_{12}} + \frac{m_1}{m_1+m_2}\frac{\partial}{\partial \vec{R}} \qquad \frac{\partial}{\partial r_2} = \frac{\partial}{\partial r_{12}} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial \vec{R}}$$

$$\hat{H}(\vec{r}_{12},\vec{R}) = -\frac{1}{2\mu}\hat{\Delta}_{r_{12}} - \frac{1}{2M}\hat{\Delta}_R + \frac{k}{2}|r_{12}|^2 \qquad \mu = \frac{m_1 m_2}{m_1+m_2}$$

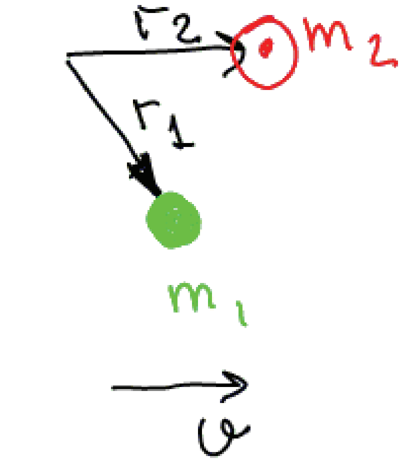
$M = m_1 + m_2$

exact solution: $\Psi = \varphi(r_{12})\,\chi(R)$

$$\varphi_{GS}(r_{12}) = \frac{(k\mu)^{3/8}}{\pi^{3/4}} e^{-\frac{1}{2}\sqrt{k\mu}\, r_{12}^2} \qquad \chi(R) = \exp(i\,\vec{p}\cdot\vec{R})$$

$$\vec{p} = M\vec{v}.$$

Electron current density in Hooke's atom



$$\vec{p} = M\vec{v}\,.$$

$$\frac{\partial}{\partial r_2} = \frac{\partial}{\partial r_{12}} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial \vec{R}}$$

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

$$M = m_1 + m_2$$

$$\Psi = \varphi(r_{12})\,\chi(R) \qquad \chi(R) = \exp(i\,\vec{p}\cdot\vec{R})$$

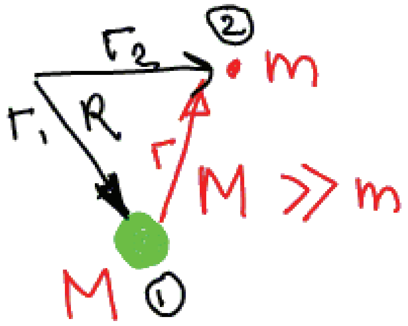
$$\varphi_{GS}(r_{12}) = \frac{(k\mu)^{3/8}}{\pi^{3/4}}\, e^{-\frac{1}{2}\sqrt{k\mu}\, r_{12}^2}$$

$$\vec{j}_2 = \frac{-1}{2m_2}\left[i\hbar\,\Psi^*\vec{\nabla}_{r_2}\Psi + c.c.\right]$$

$$= \frac{-\hbar}{2m_2}\left[\underbrace{\cancel{i\varphi^*\chi^*(-\sqrt{k\mu})\,\vec{r}_{12}\varphi\chi - \;''\;}}_{\text{terms from } \partial/\partial r_{12}} + \underbrace{i\frac{m_2}{M}\varphi^*\chi^*\, i\vec{p}\,\varphi\chi + \text{—}\,''\,\text{—}}_{\dots\text{ from } \partial/\partial\vec{R}}\right]$$

$$= \frac{\hbar\vec{p}}{M}|\Psi|^2 = \hbar\,\vec{v}\,|\Psi|^2$$

Hooke's atom (BO approximation)



$$\hat H(\vec r_1,\vec r_2) = -\frac{\hbar^2}{2M}\hat\Delta_1 - \frac{\hbar^2}{2m}\hat\Delta_2 + \frac{k}{2}|\vec r_1-\vec r_2|^2$$

$$\Psi(r_1,r_2)\approx\varphi(\vec r)\,\chi(\vec R) \longleftarrow \underline{\text{B.-O.}}$$

$$\vec r = \vec r_2 - \vec r_1 \qquad \vec R = \vec r_1 \qquad \mu = \frac{mM}{m+M}$$

$$\frac{\partial}{\partial r_1} = -\frac{\partial}{\partial r}+\frac{\partial}{\partial R} \qquad \frac{\partial}{\partial r_2} = \frac{\partial}{\partial r}$$

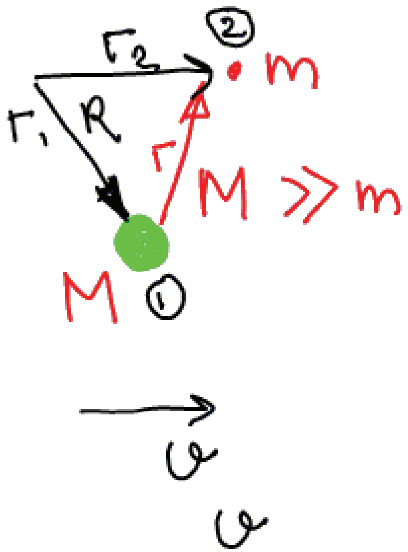
$$\hat H_{BO}(\vec r,\vec R) = -\frac{\hbar^2}{2M}\hat\Delta_R + \frac{\hbar^2}{M}\frac{\partial}{\partial\vec r}\cdot\frac{\partial}{\partial\vec R} - \frac{1}{2\mu}\hat\Delta_r + \frac{k}{2}r^2$$

$$\varphi_{BO,gs}(\vec r) = \frac{(k\mu)^{3/8}}{\pi^{3/4}}\, e^{-\frac12\sqrt{k\mu}\,r^2} \qquad \left(E_e = \frac32\sqrt{\frac{k}{\mu}}\right)$$

$$\chi(\vec R) = \exp(i\,\vec p\cdot\vec R)$$ * coordinate & momentum of the nucleus, not C.O.M.

* this is no longer an exact solution!

Current density in B.-O. Hooke's atom



$$\Psi(r_1,r_2) \approx \varphi(\vec r)\,\chi(\vec R)$$

$$\varphi_{BO,gs}(\vec r) = \frac{(k\mu)^{3/8}}{\pi^{3/4}}\, e^{-\frac{1}{2}\sqrt{k\mu}\, r^2}$$

$$\chi(\vec R) = \exp(i\,\vec p\cdot\vec R)$$

$$\frac{\partial}{\partial r_2} = \frac{\partial}{\partial r}\left[+\frac{m}{m+M}\frac{\partial}{\partial R}\right]$$

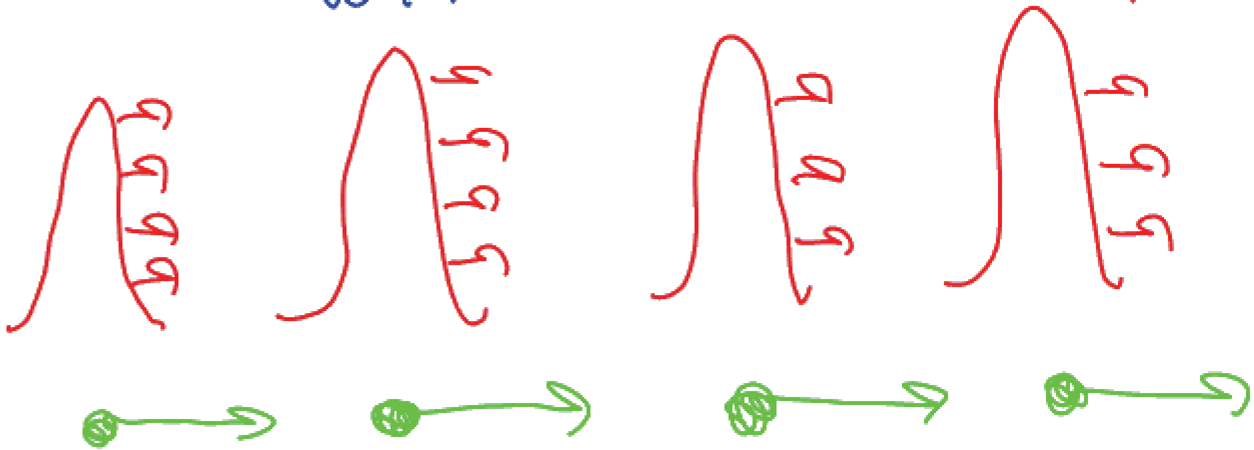
term absent in the B.O. approx.

$$\vec j_2 = \frac{-1}{2m}\left[i\hbar\,\Psi^*\vec\nabla_{r_2}\Psi + c.c.\right]$$

$$= -\frac{1}{2m}\left[\cancel{i\hbar\,\varphi^*\chi^*\left(-\sqrt{k\mu}\,\vec r\right)\varphi\chi \;-\; {}''}\right]$$

$$= 0$$

exact: electron moves with the nucleus $p_e = m_e V$

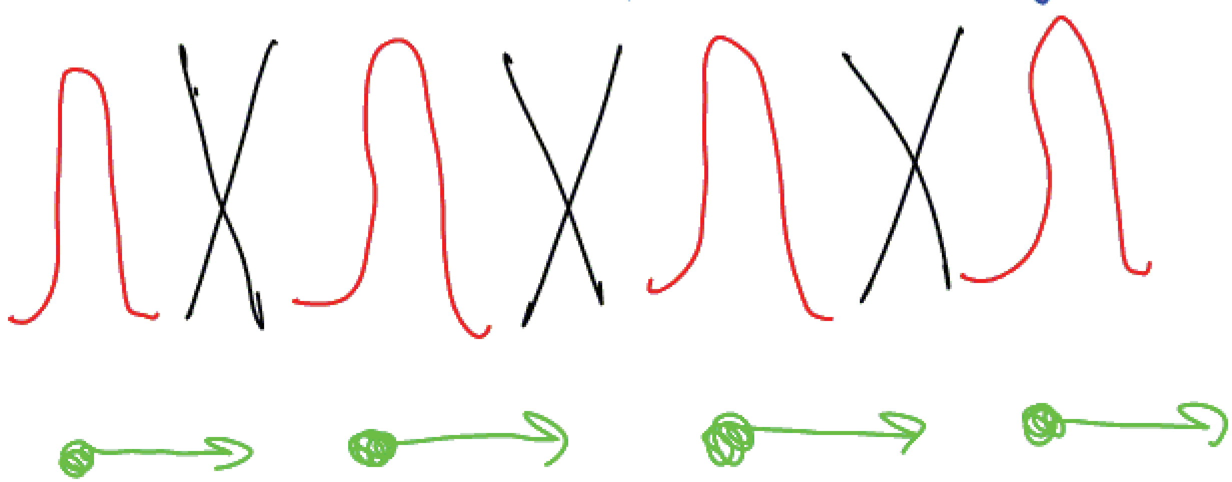


$p_n = m_n V$

time

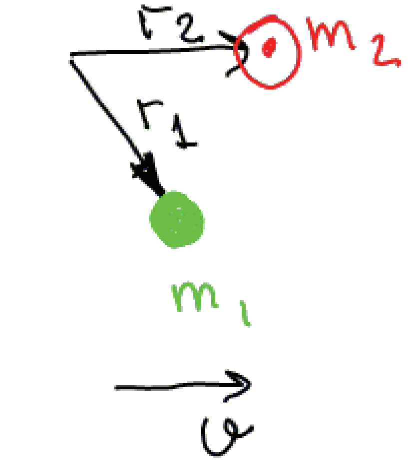
B.O.: electron disappears at the old location, and reappears at the new one

$p_e = 0$



$p_n = m_n V$

What went wrong?



$\vec{p} = M\vec{v}.$

$$\frac{\partial}{\partial r_2} = \frac{\partial}{\partial r_{12}} + \frac{m_2}{m_1+m_2}\frac{\partial}{\partial \vec{R}}$$

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

$$M = m_1 + m_2$$

$$\Psi = \varphi(r_{12})\,\chi(R) \qquad \chi(R) = \exp(i\,\vec{p}\cdot\vec{R})$$

$$\varphi_{GS}(r_{12}) = \frac{(k\mu)^{3/8}}{\pi^{3/4}}\, e^{-\frac{1}{2}\sqrt{k\mu}\, r_{12}^2}$$

$$\vec{j}_2 = \frac{-1}{2m_2}\left[i\hbar\,\Psi^*\vec{\nabla}_{r_2}\Psi + c.c.\right]$$

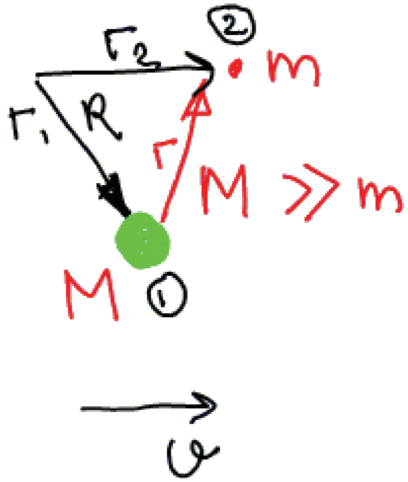
$$= \frac{-\hbar}{2m_2}\left[i\,\varphi^*\chi^*(-\sqrt{k\mu})\,\vec{r}_{12}\,\varphi\chi + i\frac{m_2}{M}\varphi^*\chi^*\, i\vec{p}\,\varphi\chi \right.$$
$$\left. - \text{———} \,''\, \text{———} + \text{———} \,''\, \text{———}\right]$$

terms from $\partial/\partial r_{12}$ vanish if φ_{GS} is real

... from $\partial/\partial\vec{R}$ vanish in B.O.

Must make φ_{GS} complex!

Recovering current in BO Hooke's atom (1)



$\alpha = \sqrt{k\mu}$

$$\hat{H}_{BO}(\vec{r},\vec{R}) = -\frac{\hbar^2}{2M}\hat{\Delta}_R + \frac{\hbar^2}{M}\frac{\partial}{\partial \vec{r}}\cdot\frac{\partial}{\partial \vec{R}} - \frac{1}{2\mu}\hat{\Delta}_r + \frac{k}{2}r^2$$

$$\Psi(r_1,r_2) \approx \varphi_1(\vec{r})\chi_1(\vec{R}) + \varphi_2(\vec{r})\chi_2(\vec{R})$$

(Born-Huang approximation)

$$\varphi_1 = \left(\frac{\alpha}{\pi}\right)^{3/4} e^{-\frac{\alpha}{2}r^2} \quad \left(E_1 = \frac{3}{2}\sqrt{\frac{k}{\mu}}\right)$$

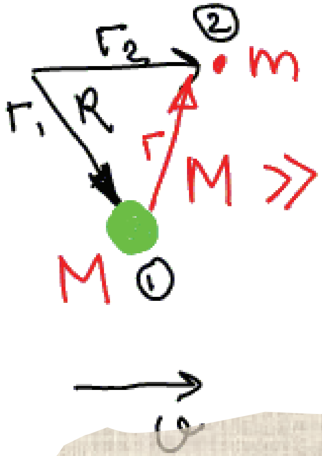
$$\varphi_2 = \frac{\sqrt{2}\,\alpha^{5/4}}{\pi^{3/4}} r_z e^{-\frac{\alpha}{2}r^2} \left(E_2 = \frac{5}{2}\sqrt{\frac{k}{\mu}}\right)$$

$$\langle \varphi_1 | \hat{H}_{BO}\Psi \rangle = \left\{-\frac{\hbar^2}{2M}\hat{\Delta}_R + E_1\right\}\chi_1 + \frac{1}{M}\sqrt{\frac{\alpha}{2}}\frac{\partial}{\partial R_z}\chi_2$$

$$\langle \varphi_2 | \hat{H}_{BO}\Psi \rangle = \left\{-\frac{\hbar^2}{2M}\hat{\Delta}_R + E_2\right\}\chi_2 - \frac{1}{M}\sqrt{\frac{\alpha}{2}}\frac{\partial}{\partial R_z}\chi_1$$

$$\chi_1 = a_1 \exp(i p R_z)\,;\quad \chi_2 = a_2 \exp(i p R_z)$$

Recovering current in BO Hooke's atom (2)



$M \gg m$

$$\langle \varphi_1 | \hat{H}_{BO} \Psi \rangle = \left\{ -\frac{\hbar}{2M}\Delta_R + E_1 \right\}\chi_1 + \frac{1}{M}\sqrt{\frac{\alpha}{2}}\frac{\partial}{\partial R_z}\chi_2$$

$$\langle \varphi_2 | \hat{H}_{BO} \Psi \rangle = \left\{ -\frac{\hbar^2}{2M}\hat{\Delta}_R + E_2 \right\}\chi_2 - \frac{1}{M}\sqrt{\frac{\alpha}{2}}\frac{\partial}{\partial R_z}\chi_1$$

$$\chi_1 = a_1 \exp(ipR_z)\ ; \quad \chi_2 = a_2 \exp(ipR_z)$$

This is a "Complete Adiabatic" wavefunction [L. Nafie, JCP 79, 4950 (1983)]

$\alpha = \sqrt{k\mu}$

$$\begin{cases} a_1\left\{\frac{p^2}{2M} + E_1 - \varepsilon\right\} + \frac{ip\sqrt{\alpha}}{\sqrt{2}\,M}a_2 = 0 \\ -\frac{ip\sqrt{\alpha}}{\sqrt{2}\,M}a_1 + \left\{\frac{p^2}{2M} + E_2 - \varepsilon\right\}a_2 = 0 \end{cases} \Rightarrow$$

for small v

$$a_1 \approx 1$$

$$a_2 \approx -i\left(\frac{\mu v^2}{2\Delta E}\right)^{1/2}$$

$$\Psi_{BH}(\vec{r}, \vec{R}, \vec{p}) \approx e^{ipR_z}\frac{\alpha^{3/4}}{\pi^{3/4}}e^{-\frac{\alpha}{2}r^2}\left\{1 - i\, r_z \mu^{1/2} v_z\right\}$$

$\Rightarrow$ this gives the correct current

We understand what's going on.
Can we fix up the general B.-O. / B.-H. current density in a similar way?

Reminder: the Born-Huang approximation

$$\hat{H}(\{r_i\};\{R_a\};t) = \sum_i^n -\frac{\hbar^2}{2m_i}\hat{\Delta}_i + \sum_a^N \frac{\hbar^2}{2M_a}\hat{\Delta}_a + v(\{r_i\};\{R_a\}) + v_t(\{r_i\};\{R_a\};t)$$

$$\Psi(\{r_i\};\{R_a\};t) = \sum_\mu^c \psi_\mu(\{r_i\};\{R_a\})\,\chi_\mu(\{R_a\};t)$$

$$\hat{H}_{el}\,\psi_\mu(\{r_i\};\{R_a\}) = v_\mu(\{R_a\})\,\psi_\mu(\{r_i\};\{R_a\})$$

$$\hat{H}_{el} = \sum_i^n -\frac{\hbar^2}{2m_i}\hat{\Delta}_i + v(\{r_i\};\{R_i\})$$

$$i\hbar\frac{\partial}{\partial t}\chi_\nu = \sum_a^N -\frac{\hbar^2}{2M_a}\hat{\Delta}_a\chi_\nu + \sum_\mu v_{\nu\mu}\chi_\mu + \sum_\mu\sum_a \vec{g}_{\nu\mu a}\frac{\partial}{\partial \vec{R}_a}\chi_\mu$$

$$v_{\nu\mu}(\{R_a\};t) = \delta_{\mu\nu}v_\mu + \langle\psi_\nu|\, v_t + \sum_a -\frac{\hbar^2}{2M_a}\Delta_a\,|\psi_\mu\rangle$$

$$\vec{g}_{\nu\mu a}(\{R_b\}) = -\frac{\hbar^2}{2M_a}\langle\psi_\nu|\frac{\partial}{\partial \vec{R}_a}|\psi_\mu\rangle \qquad \Big|\; \vec{g}_{\nu\mu a} = -\vec{g}^{\,*}_{\mu\nu a}$$

Our assumptions:

- We already have a time-dependent Born-Huang solution, which includes all electronic states important for describing the density evolution:

$$\Psi(\{r_i\};\{R_a\};t) = \sum_{\mu}^{c} \Psi_\mu(\{r_i\};\{R_a\})\chi_\mu(\{R_a\};t)$$

- Amplitudes of the additional "correction" electronic states are adiabatic w.r.t. nuclear coordinates
- Amplitudes of the "correction" states are small compared to the explicitly included states
- Indirect coupling between the explicit electronic surfaces due to interaction with the "correction" states can be neglected

$$\Psi(\{r_i\};\{R_a\};t) = \sum_{\mu}^{c} \left\{ \Psi_\mu + \sum_{\lambda > c}^{\infty} a_{\mu\lambda}(\{R_a\};t)\Psi_\lambda \right\} \chi_\mu(\{R_a\},t)$$

Solving for the correction w.f.s

$$i\hbar\frac{\partial}{\partial t}\chi_\nu = \sum_a^N -\frac{\hbar^2}{2M_a}\hat{\Delta}_a\chi_\nu + \sum_\mu \vartheta_{\nu\mu}\chi_\mu + \sum_\mu\sum_a \vec{g}_{\nu\mu a}\cdot\frac{\partial}{\partial\vec{R}_a}\chi_\mu$$

$$\Psi(\{r_i\};\{R_a\};t) = \sum_\mu^{c}{}' \left\{\Psi_\mu + \sum_{\lambda>c}^{\infty} a_{\mu\lambda}(\{R_a\};t)\Psi_\lambda\right\}\chi_\mu(\{R_a\},t)$$

for $\nu > c$: adiabaticity! ? currents are small!

$$i\hbar\frac{\partial}{\partial t}\left(\sum_\mu^{c}{}' a_{\mu\nu}\chi_\mu\right) = \left(\sum_a^N -\frac{\hbar^2}{2M_a}\hat{\Delta}_a\right)\sum_\mu^{c} a_{\mu\nu}\chi_\mu + \cancel{\sum_\mu^{c}\vartheta_{\nu\mu}\chi_\mu} + \vartheta_{\nu\nu}\sum_\mu^{c} a_{\mu\nu}\chi_\mu + \sum_\mu^{c}{}'\sum_a \vec{g}_{\nu\mu a}\cdot\frac{\partial}{\partial\vec{R}_a}\chi_\mu$$

neglect

available from B.H.: $\left(i\hbar\frac{\partial}{\partial t} + \sum_a \frac{\hbar^2}{2M_a}\hat{\Delta}_a\right)\chi_\mu = \sum_\lambda^{c}{}' \vartheta_{\mu\lambda}\chi_\lambda + \sum_\lambda^{c}\sum_a \vec{g}_{\mu\lambda a}\cdot\frac{\partial}{\partial R_a}\chi_\lambda$

Correction amplitudes

$$\sum_{\mu}^{c} a_{\mu\nu} \left\{ \sum_{\lambda}^{c} \vartheta_{\mu\lambda} \chi_\lambda - \vartheta_{\nu\nu} \chi_\mu + \sum_{\lambda}^{c} \sum_{a} \vec{g}_{\mu\lambda a} \cdot \frac{\partial}{\partial R_a} \chi_\lambda \right\}$$

$$= \sum_{\mu}^{c} \sum_{a} \vec{g}_{\nu\mu a} \cdot \frac{\partial}{\partial \vec{R}_a} \chi_\mu \qquad \Big| \; \vec{g}_{\nu\mu a} = -\frac{\hbar^2}{2M_a} \times \langle \Psi_\nu | \frac{\partial}{\partial R_a} | \Psi_\mu \rangle$$

This is a point-wise in $\{\vec{R}\}$ system of linear equations. Away from state crossings, this simplifies to:

$$a_{\mu\nu} \chi_\mu = -\frac{1}{\vartheta_{\nu\nu} - \vartheta_{\mu\mu}} \sum_{a}^{N} \vec{g}_{\nu\mu a} \cdot \frac{\partial}{\partial \vec{R}_a} \chi_\mu$$

(also holds for a single B.O. surface).

on B.O. surface: $\underbrace{}_{\text{real}}$ $\underbrace{}_{\text{real}}$ $\underbrace{}_{\text{real if stationary}}$

Electron currents

$$\bar{\Psi}(\{r_i\};\{R_a\};\{P_a\},t) = \sum_{\mu}^{c}\left\{\psi_\mu + \sum_{\lambda>c}^{\infty} a_{\mu\lambda}(\{R_a\};t)\psi_\lambda\right\}\chi_\mu(\{R_a\},t)$$

$$\vec{j}(\{r_i\};\{R_a\}) = -\frac{i\hbar e}{2m_e}\left(\bar{\Psi}^*\sum_i^n \frac{\partial}{\partial \vec{r}_i}\bar{\Psi} - c.c.\right)$$

$$\sum_i^n \frac{\partial}{\partial \vec{r}_i}\psi_\mu + \sum_a^N \frac{\partial}{\partial \vec{R}_a}\psi_\mu = 0 \qquad \sum_a^N \frac{\partial}{\partial \vec{R}_a} \equiv \hat{G}$$

N.B. neglect terms quadratic in $a_{\mu\lambda}$!

This is a "Complete Adiabatic" wavefunction [L. Nafie, JCP 79, 4950 (1983)]

$$\left(\sum_i \frac{\partial}{\partial \vec{r}_i}\right)\bar{\Psi} = -\sum_\mu^c \chi_\mu \left(\sum_a^N \frac{\partial}{\partial \vec{R}_a}\psi_\mu\right) - \sum_{\lambda>c}\left(\sum_a \frac{\partial}{\partial \vec{R}_a}\psi_\lambda\right)\times\sum_\mu^c (a_{\mu\lambda}\chi_\mu)$$

$$\vec{j} = \frac{i\hbar e}{2m_e}\sum_{\mu\lambda}^{c}\left[\chi_\lambda^*\chi_\mu\psi_\lambda^*\hat{G}\psi_\mu - \chi_\lambda\chi_\mu^*\psi_\lambda\hat{G}\psi_\mu^*\right]$$

$$+\frac{i\hbar e}{2m_e}\sum_\mu^c\sum_{\tau>c}^{\infty}\sum_\lambda^c\left[\begin{array}{l} a_{\lambda\tau}^*\chi_\lambda^*\chi_\mu\psi_\tau^*\hat{G}\psi_\mu - c.c. \\ -a_{\lambda\tau}^*\chi_\lambda^*\chi_\mu\psi_\mu\hat{G}\psi_\tau^* + c.c. \end{array}\right]$$

Electron currents – some special cases

multiple surfaces, real $\Psi_\lambda \equiv \Phi_\lambda$:

$$j = \frac{i\hbar e}{2m_e} \sum_{\mu\lambda}^{e}{}' (\chi^*_\lambda \chi_\mu - \chi_\lambda \chi^*_\mu) \Phi_\lambda \hat{G} \Phi_\mu$$

$$+ \frac{i\hbar e}{2m_e} \sum_{\mu} \sum_{\tau > e}^{\infty}{}' \sum_{\lambda}^{e}{}' (a^*_{\lambda\tau} \chi^*_\lambda \chi_\mu - c.c.)(\Phi_\tau \hat{G} \Phi_\mu + \Phi_\mu \hat{G} \Phi_\tau)$$

single B.O. surface, real w.f.s:

$$j = \frac{i\hbar e}{2m_e} \sum_{\tau > 1}^{\infty} (a^*_{1\tau} - a_{1\tau}) \chi^*_1 \chi_1 (\Phi_\tau \hat{G} \Phi_1 + \Phi_1 \hat{G} \Phi_\tau)$$

$$j = \frac{i\hbar e}{2m_e} \sum_{\tau > 1}^{\infty} (\Phi_\tau \hat{G} \Phi_1 + \Phi_1 \hat{G} \Phi_\tau) \frac{1}{\epsilon_{0\tau} - \epsilon_{11}} \sum_a^N \vec{g}_{\tau 1 a} \cdot \left(\chi^*_1 \frac{\partial}{\partial \vec{R}_a} \chi_1 - c.c.\right)$$

$$\hat{G} = \sum_a^N \frac{\partial}{\partial \vec{R}_a} \; ; \; \vec{g}_{\nu\mu a}(\{R_b\}) = -\frac{\hbar^2}{2M_a} \langle \Psi_\nu | \frac{\partial}{\partial \vec{R}_a} | \Psi_\mu \rangle$$

Impractical theory (single-surface)

$$\vec{j} \approx \frac{i\hbar e}{2mc} \sum_{v>1}^{\infty} \left(\Psi_v \hat{G} \Psi_1 + \Psi_1 \hat{G} \Psi_v \right) \frac{1}{\vartheta_{0v} - \vartheta_{11}} \sum_{a}^{N} \vec{g}_{v1a} \cdot \left(\chi_1^* \frac{\partial}{\partial \vec{R}_a} \chi_1 - c.c. \right)$$

$$\hat{G} = \sum_{a}^{N} \frac{\partial}{\partial \vec{R}_a} \; ; \quad \vec{g}_{v\mu a}(\{R_b\}) = -\frac{\hbar^2}{2M_a} \left\langle \Psi_v \right| \frac{\partial}{\partial \vec{R}_a} \left| \Psi_\mu \right\rangle$$

This expression is cute, but numerically useless: the largest contributions to the current come from coupling to the core-excited states.

For any chemically interesting system, these would be too expensive to calculate

(implemented by Freedman et al, JACS 119, 10620 (1997) for a non-interacting w.f.)

Another impractical theory (single-surface)

$$\vec{j}_e(\{r_i\},\{R_a\},t) = \rho_N \vec{j}_{11} + 2\sum_{\lambda>1} \frac{1}{\vartheta_{\lambda\lambda}-\vartheta_{11}} \left\{ \frac{i}{\hbar} \sum_b^N \mathrm{Re}(\vec{g}_{\lambda 1 b}) \cdot \vec{P}_b \right\} \vec{j}_{\lambda 1}$$

$$\rho_N(\{R_a\},t) = \chi_1^* \chi_1$$

nuclear probability density

$$\vec{P}_b(\{R_a\},t) = \frac{i\hbar}{2} \left\{ \chi_1 \left(\frac{\partial}{\partial \vec{R}_b} \chi_1^* \right) - \chi_1^* \left(\frac{\partial}{\partial \vec{R}_b} \chi_1 \right) \right\}$$

nuclear momentum density

$$\vec{j}_{\lambda 1}(\{\vec{r}_i\},\{\vec{R}_a\}) = \frac{i\hbar}{2} \left[\Psi_1 (\hat{G} \Psi_\lambda^*) - \Psi_\lambda^* (\hat{G} \Psi_1) \right]$$

electron transition current

$$\hat{G} = \frac{1}{m_e} \sum_i^n \frac{\partial}{\partial \vec{r}_i}$$

all matrix elements are Hermitian

Practical theory (2nd order)

$$\vec{j}_e(\{r_i\},\{R_a\},t) = \underset{0\,=}{\cancel{\rho_N \vec{j}_{11}}} + 2\sum_{\lambda>1} \frac{1}{\vartheta_{\lambda 1}-\vartheta_{11}} \left\{\frac{i}{\hbar}\sum_b^N \mathrm{Re}(\vec{g}_{\lambda 1 b})\cdot\vec{P}_b\right\}\vec{j}_{\lambda 1}$$

$$\vec{g}_{\lambda 1 b}(\{\vec{R}_a\}) = -\frac{\hbar^2}{M_b}\left\langle\Psi_\lambda\left|\frac{\partial}{\partial \vec{R}_b}\right|\Psi_1\right\rangle$$

$$\vec{j}_{\lambda 1}(\{\vec{r}_i\},\{\vec{R}_a\}) = \frac{i\hbar}{2}\left[\Psi_1(\hat{G}\Psi_\lambda^*) - \Psi_\lambda^*(\hat{G}\Psi_1)\right]$$

$$\vec{j}_e = \frac{\partial}{\partial\lambda_1\partial\lambda_2} E\left[\hat{H}_{BO} + \lambda_1\hat{H}_1 + \lambda_2\hat{H}_2\right]$$

$$\hat{H}_1 = -i\hbar\sum_b^N \vec{V}_b\cdot\frac{\partial}{\partial\vec{R}_b} \qquad \vec{V}_b = \frac{\vec{P}_b}{M_b}$$

$$\hat{H}_2(\{r_i\}) = \frac{i\hbar}{2m_e}\left[\left\{\sum_j^n \overleftarrow{\frac{\partial}{\partial \vec{r}_j}}\right\}\delta(\{r_j\}-\{r_i\}) - \delta(\{r_j\}-\{r_i\})\left\{\sum_j^n \frac{\partial}{\partial\vec{r}_j}\right\}\right]$$

Practical theory (1st order)

$$\vec{j}_e = \frac{\partial^2}{\partial\lambda_1\partial\lambda_2} E\left[\hat{H}_{BO} + \lambda_1 \hat{H}_1 + \lambda_2 \hat{H}_2\right]$$

2nd derivatives are too much work

$$\hat{H}_1 = -i\hbar \sum_b^N \vec{V}_b \cdot \frac{\partial}{\partial \vec{R}_b} \qquad \vec{V}_b = \frac{\vec{P}_b}{M_b}$$

$$\hat{H}_2(\{r_i\}) = \frac{i\hbar}{2m_e}\left[\left\{\sum_j^n \frac{\overleftarrow{\partial}}{\partial \vec{r}_j}\right\}\delta(\{r_j\}-\{r_i\}) - \delta(\{r_j\}-\{r_i\})\left\{\sum_j^n \frac{\partial}{\partial \vec{r}_j}\right\}\right]$$

$$\vec{j}_e \approx \frac{\partial}{\partial\lambda_2} E\left[\hat{H}_{BO} + \hat{H}_1 + \lambda_2 \hat{H}_2\right]$$

$$= \left\langle \Psi[\hat{H}_{BO} + \hat{H}_1] \middle| \hat{H}_2 \middle| \Psi[\hat{H}_{BO} + \hat{H}_1] \right\rangle$$

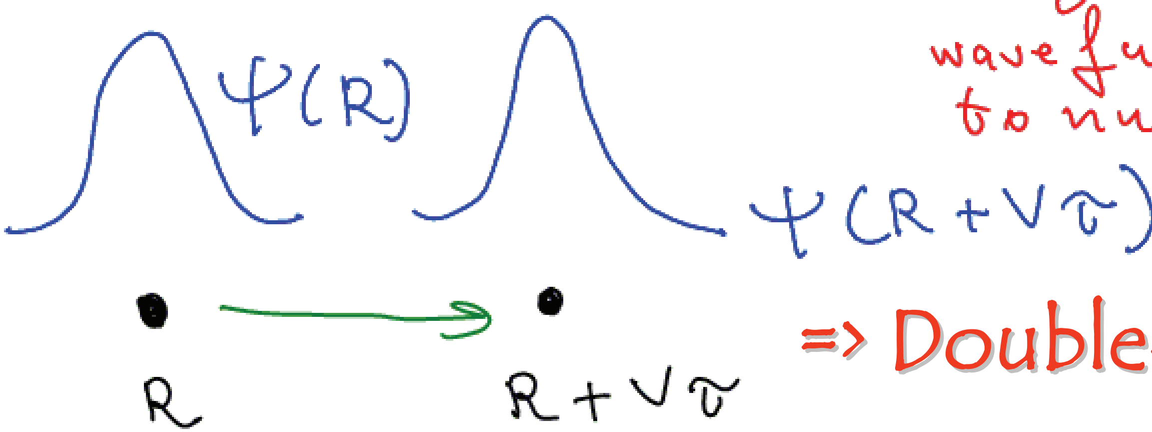
Hellmann-Feynman

This is a "Complete Adiabatic" wavefunction [L. Nafie, JCP 79, 4950 (1983)]

Nitty-gritty: Evaluating Complete Adiabatic w.f.

$\Psi_{CA}\left[\hat{H}_{BO}+\hat{H}_1\right]$ $\qquad \hat{H}_1 = -i\hbar \sum_b^N \vec{V}_b \cdot \frac{\partial}{\partial \vec{R}_b}$

Requires 1st order wavefunction response to nuclear displacement.

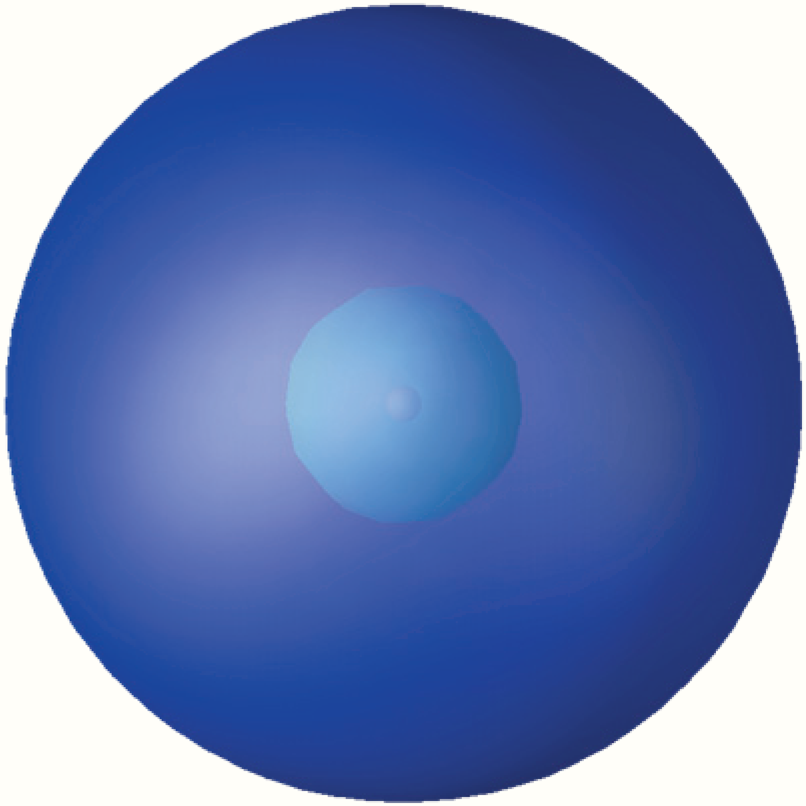


=> Double-SCF procedure

$$h_{ij}^{(1)} \approx -\frac{i\hbar}{\tau}\left[\langle \varphi_i(\{R_b\}) | \varphi_j(\{R_b+V_b\tau\})\rangle - \delta_{ij}\right]$$

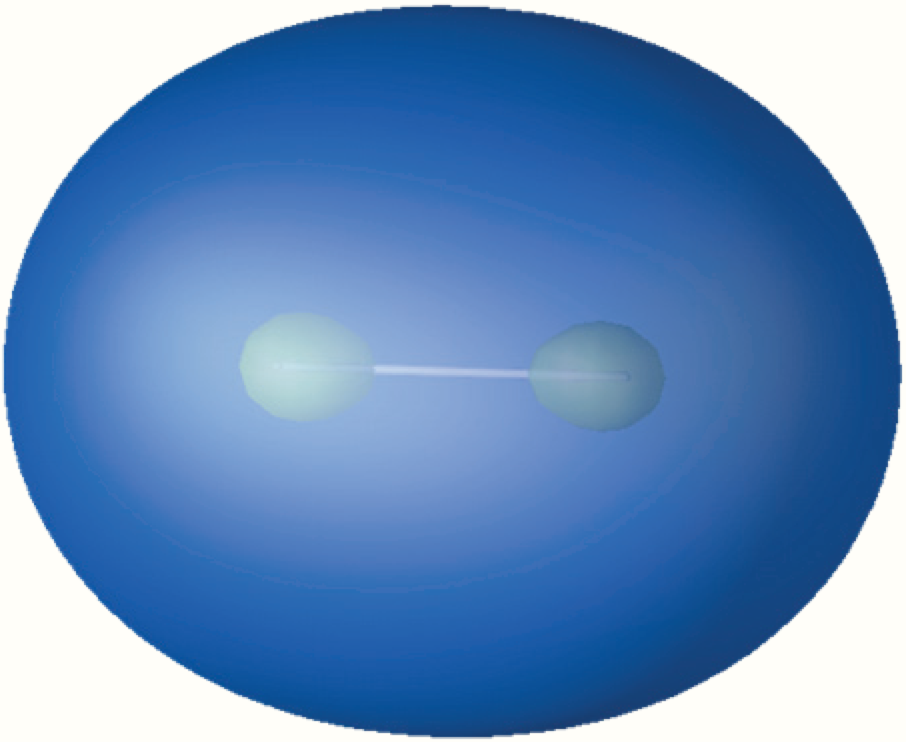
(single-particle matrix elements)

A very boring example



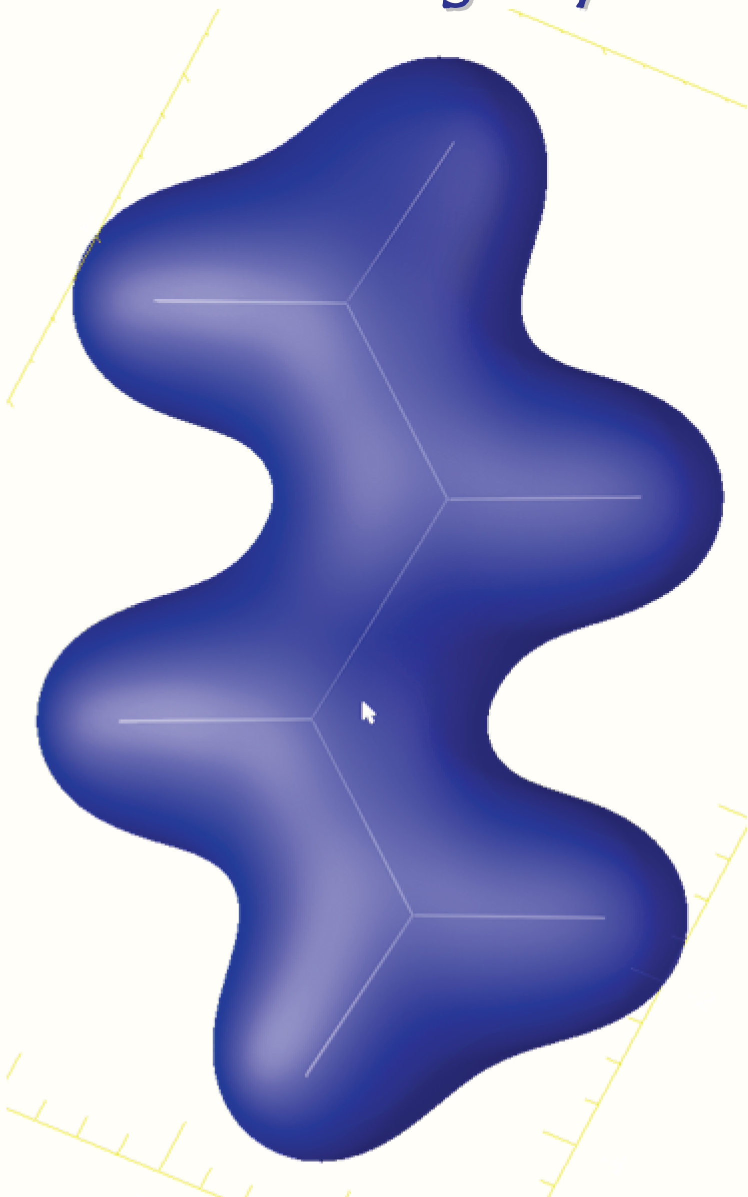
- He atom
- Moving towards positive X at 0.01 Bohr/au[t] (22 km/s)
- Saturated basis set

Another boring example



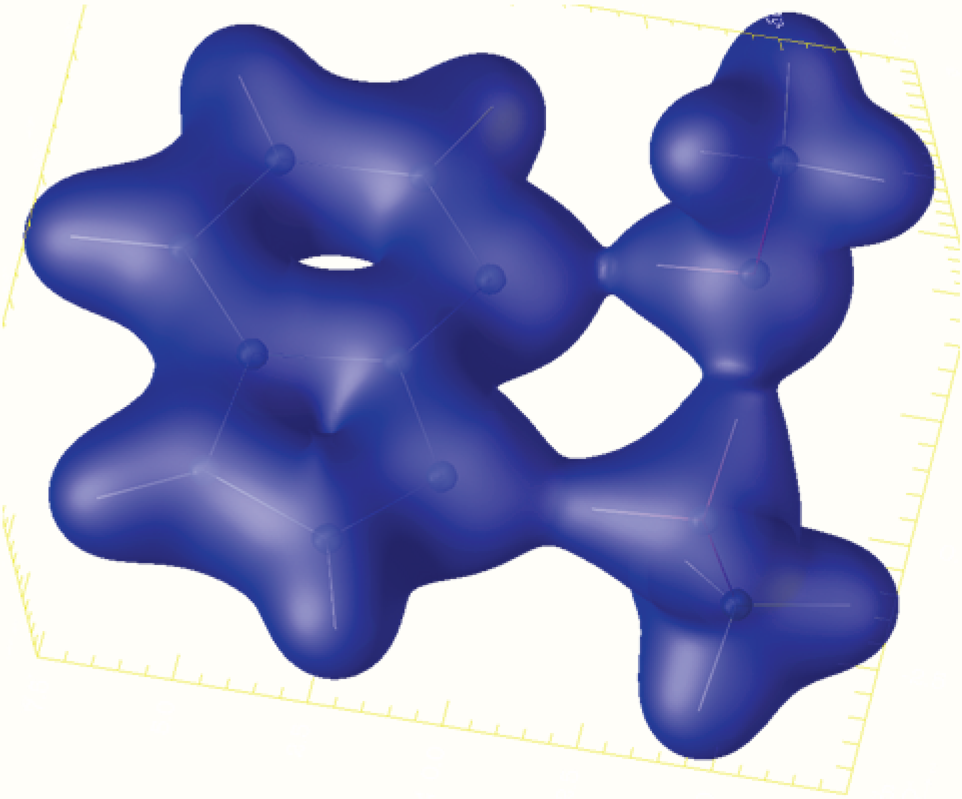
- H_2 molecule
- Rotating around Y axis at 0.029 Rad/au[t] (E_{rot}=20 eV; J=50)
- "pc-3" polarization-consistent basis set

(Slightly) less boring example



- Butadiene (C_4H_6) molecule
- Central carbon atoms (C_2 and C_3) moving towards C.o.M. at 0.01 Bohr/au[t] (22 km/s)
- "pc-1" polarization-consistent basis set

Real chemistry example



- 7-azaindole + 2x methanol
- Transition structure for proton transfer
- Nuclei are moving along the Intrinsic Reaction coordinate (arb. velocity)
- "pc-1" polarization-consistent basis set

Conclusions

- Born-Oppenheimer wavefunctions of molecules in motion yield zero electron currents, which do not satisfy continuity relations for electron density
- B.-O. wavefunctions are not Lorentz-invariant
- Currents be recovered within Born-Huang Ansatz, leading to the Nafie's Complete Adiabatic wavefunctions
- Electron currents are the 1+2-order derivative of the B.-O. electronic energies
- C.A. wavefunctions and electron currents can be obtained by a simple double-SCF procedure
- C.A. wavefunctions provide the natural representation of femtosecond dynamics

Thank you for listening!